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Toward an understanding of the nonlinear nature of atmospheric photochemistry: Origin of the complicated dynamic behaviour of the mesospheric photochemical system

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Abstract. The methods of nonlinear dynamics are used to reveal the origin of complicated dynamic behavior (CDB) of a dynamic model of the mesospheric photochemical system (PCS) perturbed by diurnal variations in photolysis rates. We found that CDB appearance during the multi-day evolution is unambiguously determined by two peculiarities in the model behavior during its 24-hours evolution. These peculiarities are the presence of a stage of abrupt changes in reagent concentrations and the "humped" dependence of the end-night atomic hydrogen concentrations on those at the beginning of the night. Using a successive analysis we found that these two peculiarities are, in turn, conditioned by the specific features of the chemical processes involved in the model, namely, by the catalytic cycle whose net rate is independent of the concentration of the destroyed species (here, it is atomic oxygen). We believe that similar peculiarities inherent in other atmospheric PCSs indicate that under appropriate conditions they may also demonstrate CDB. We identified the mechanism of the CDB appearance and described it in two ways. The first one reveals a sequence of the processes causing the exponential (on the average) growth of a perturbation of the solution with time. In particular, we found that the behavior of small perturbations of an arbitrary solution of model equations is identical to the behavior of a linear oscillator excited parametrically. The second way shows the mechanism of CDB appearance by means of 1-dimensional mapping, which is, basically, the same as the well-known Feigenbaum mappings.

1 Introduction

One of the key issues in investigations concerned with the physics and chemistry of the atmosphere is related to human- influenced and natural changes in chemical composition of the atmosphere. This is due, primarily, to a deeper understanding of numerous links between chemical properties of the atmosphere and the environment characteristics (see, e.g., WMO, 1995, and the cited literature).

The composition of the atmosphere and its changes are, to a great extent, determined by a number of chemical reactions, including reactions of photolysis. Sets of these reactions determining the composition of air in various definite regions of the atmosphere constitute atmospheric photochemical systems (PCSs). The dynamics of atmospheric photochemical systems, that is, changes of the chemical composition in time due to photochemical processes, is known to be described by sets of a great number of nonlinear differential or integrodifferential equations (balance equations) for concentrations of minor constituents of the atmosphere (see, e.g., Brasseur and Solomon, 1984). It can be expected that nonlinearity of these systems may manifest itself through the presence of distinctive features in their behavior, such as self-oscillations, multistability, or chaotic oscillations, which are inherent in various nonlinear dynamic systems independent of their nature. However, the long-standing experience of elaboration and verification of the models describing the atmospheric chemical composition bears evidence that such manifestations are very rare; so the possibility of the manifestations of the nonlinear nature of atmospheric photochemical systems is implicitly neglected in most studies of atmospheric chemical composition. Rareness of the nonlinear effects in atmospheric PCSs is, no doubt, a consequence of the fact that such systems are strongly dissipative in their nature. The processes involved in the atmospheric PCSs generally tend to diminish any arbitrary perturbation of reagent concentrations, and monotonously lead the system to a single equilibrium regime. Nevertheless, special modeling studies provide arguments that various atmospheric PCSs under definite conditions may indeed possess multiple equilibrium states (Prather et al., 1979; Fox et al., 1982; White and Dietz, 1984; Kasting and Ackerman, 1985; Stewart, 1993, Yang

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and Brasseur, 1994; Konovalov et al., 1998), self-oscillations (Madronich and Hess, 1994; Krol, 1995; Stewart, 1995; Feigin and Konovalov, 1995, 1996; Poppe and Lustfeld, 1996; Hess and Madronich, 1997; Krol and Poppe, 1998), and subharmonic and chaotic regimes forced by diurnal variations of photolysis rates (Fichtelmann and Sonnemann, 1992; Sonnemann and Fichtelmann, 1997). The dynamic behavior corresponding to such situations is referred to below as the complicated dynamic behavior (CDB).

The noted possibilities of CDB may be a reason for abrupt changes in variable values of PCSs, that is, concentrations of chemical species caused by insignificant changes of parameter values. Feigin and Konovalov (1996) and Konovalov et al. (1998) were the first to demonstrate such an opportunity on an example of real natural phenomenon. They presented arguments that the CDB of the high-latitude lower stratospheric photochemical system, associated with the presence of self-oscillations and multiple equilibrium states, is a deep reason for both the steepness of the development of the ozone depletion in the Antarctic region in mid 1980s and the abnormally low ozone concentrations observed in spring Antarctic stratosphere during the ozone hole phenomenon. Kleinman (1991, 1994) considered the presence of two qualitatively different regimes in the tropospheric photochemistry, whose realization depends strongly on the values of some parameters, and argued that these regimes can be observed indeed. He did not establish direct links between the existence of the different chemical regimes and possibilities of CDB of the tropospheric PCS, so additional investigations are needed to identify manifestations of CDB of the tropospheric PCS in observations. Nevertheless, we consider his results to be an evidence that such manifestations are quite plausible. It is necessaty to predict possible abrupt changes in chemical composition of the atmosphere that, in our opinion, proves an importance of the investigations aimed at revealing the situations and conditions under which CDB of the atmospheric PCSs can take place.

When CDB is revealed in some models of atmospheric PCSs (see the references given above), there arises a problem concerning its origin. We believe that a deeper understanding of the origin of CDB in the models of atmospheric PCSs may promote such investigations significantly. By the "origin" we mean here (1) various peculiarities of the system which can provoke its CDB, and (2) the mechanisms of the birth of CDB, that is sequences of basic processes (both chemical and "dynamic" in nature) causing the appearance of CDB. We believe that an understanding of the origin of CDB (1) will confirm that the CDB revealed in some model is not merely a consequence of some approximation used in the model, but is a real property of a modeled system, and (2) may provide some indicators which can be used for revealing CDB both in the nature and in models of various atmospheric PCSs.

Some aspects of the problem of interest were considered for the first time by Fox et al. (1981) in connection with multistability of their model of the stratospheric PCS. In particular, they noted that their reaction scheme provided an autocatalytic production of some species. Stewart (1995) underlined a significant role of autocatalysis for the self-oscillating regime in the model of the tropospheric PCS. Feigin and Konovalov (1995, 1996), and Konovalov et al., (1999) demonstrated the responsibility of autocatalytic processes for CDB of the high-latitude lower stratospheric PCS.

The objective of this paper is to reveal the origin of the CDB that was found by Fichtelmann and Sonnemann (1987, 1992) in their model of the mesospheric PCS. Various types of CDB (subharmonic oscillations, cascade of period doubling, and chaotic oscillations) arise in this model only owing to the periodic parametric modulation associated with diurnal variations of the photolysis rates. In other words, in the absence of periodic modulation the modeled system behaves as quite an ordinary "stable" PCS. The validity of the last remark is supported by the analysis presented in this paper and, partly, in the recent paper by Feigin et al. (1998). Note that we failed to find analogous cases not only in atmospheric chemistry but in "laboratory" chemistry too, although there are a lot of studies of chemical instabilities (see, e.g., Field and Burger, 1985). The noted peculiarity of CDB of the mesospheric PCS gives us grounds to suppose that the mechanisms of CDB of the mesospheric PCS essentially differ from those of both the atmospheric PCSs and the laboratory chemical systems demonstrating CDB under constant parameter values.

As far as we know, direct observations of CDB of the mesospheric PCS have not been made yet. The main difficulty consists in the need to obtain rows of observational data with both high temporal (less than one hour) and vertical space (less than one-two kilometers) resolutions. However, it is conceivable that the possibility of CDB of the mesospheric PCS could be indirectly confirmed after special investigations. For example, Fichtelman and Sonnemann (1992) suggested a hypothesis that two-day variations of a heating rate of the air, determined by the thermal energy released in chemical reactions in the process of two-day oscillations of the minor constituents in the mesopause region, are the trigger for excitation of the well-known quasi-two-day waves (see, e.g., Thayaparan et al., 1997; Ward et al., 1997). Some additional facts supporting the hypothesis have been provided in the recent studies by Sonnemann and Feigin (1999a, b). They have studied the dynamic behavior of a model which includes a process of eddy diffusion together with the photochemical processes and found that the model can retain the two-day oscillations even with real values of an eddy diffusion coefficient. From our viewpoint, a corroboration of the above hypothesis after special modeling studies would provide a strong support of the possibility of CDB of the real mesospheric PCS. Naturally, such studies require employing much more complex models than the original model by Fichtelman and Sonnemann (1992). In our opinion, before applying complex models it would be extremely useful to understand and estimate the effects caused by various factors not involved in the model by Fichtelman and Sonnemann

(1992) but available in the real atmosphere. Such an understanding and estimations would increase a degree of reliability of the model's results and might point to the physical and chemical factors that are the most important for CDB. We believe that the first step to be made is to reveal the origin of CDB of the mesospheric PCS.

So analysis of the origin of CDB of the mesospheric PCS appears to be important for the following reasons. (1) We believe that an understanding of the origin of CDB of the model of the mesospheric PCS will promote the investigations aimed at revealing CDB of the real mesospheric PCS. (2) Nearly all photochemical systems are subject to periodic, or quasi-periodic parametric modulations of different nature (e.g., diurnal and seasonal variations of photolysis rates and temperature, and wave motions). Thus, by studying the mesospheric PCS we are looking for indicators of the potentiality of CDB, which can be used for studying the effects of parametric modulations in other atmospheric PCSs. (3) We hope that clarification of the origin of CDB of the mesospheric PCS may give an impetus to a successful search of similar effects in nonatmospheric applications of chemistry.

The initial step of our study was development of the mesospheric PCS model (hereinafter referred to as the original model), which is very similar to the one used by Fichtelmann and Sonnemann (1992) in both the involved photochemical processes and the dynamic properties. The next principal step was a significant simplification of this model. These steps were realized in the framework of our previous study of the mesospheric photochemistry (Feigin et al., 1998) (referred to below as FKM). As a result of the simplification of the original model in accordance with the procedure developed in FKM, we have elaborated a model referred to as an essential dynamic model of the mesospheric PCS. This model possesses the principal qualitative dynamic properties (the possibility of subharmonic and chaotic oscillations and the presence of specific sequences of bifurcations of transition between different dynamic regimes) of the original model. At the same time, the essential dynamic model provides a much simpler description of the dynamics. It is the use of the essential dynamic model that allows us to solve the problem specified in this research. A brief description of both the original and essential dynamic models and their dynamic properties is presented in Sect. 2 of this paper. In Sect. 3 we apply the traditional approaches of qualitative analysis of nonlinear dynamic systems to studying the essential dynamic model with the purpose to reveal both the peculiarities of the mesospheric PCS behavior in the course of one-day variations, which are responsible for the CDB manifested on the longer time scales, and the mechanism of the appearance of CDB. In Sect.4 the knowledge of the behavior of the system is used for identification of the peculiarities of the chemical processes involved in the model, that is, reactions and reaction chains which are an integral part of the mechanism of CDB origination. Possible applications of this study along with brief formulation of the main results are presented in Sect. 5 devoted to concluding remarks. In Appendix we apply the knowledge gained in this study to derivation of analytical expressions determining the region of the parameter values in which the system possesses NDB.

Table 1. Reactions and their rate coefficients taken into account in the original model

	Reaction	Reaction rates
(R1)	$H+HO_2 \rightarrow H_2O+O$	2.40×10^{-12}
(R2)	$H+HO_2 \rightarrow H_2+O_2$	5.6×10^{-12}
(R3)	$OH+HO_2 \rightarrow H_2O+O_2$	1.80×10^{-10}
(R4)	$OH+O \rightarrow H+O_2$	4.15×10^{-11}
(R5)	$HO_2+O \rightarrow OH+O_2$	8.64×10^{-11}
(R6)	$H+O_2+M \rightarrow HO_2+M$	3.83×10^{-4}
(R7)	$H_2O+h\nu \rightarrow H+OH$	8.50×10^{2}
(R8)	$O_2+h\nu \rightarrow 2O$	2.43×10^{5}
(R9)	$O+O_2+M \rightarrow O_3+M$	5.90×10^{-6}
(R10)	$O+O_3 \rightarrow 2O_2$	1.48×10^{-16}
(R11)	$O+O+M \rightarrow O_2+M$	2.00×10^{-18}
(R12)	$H+O_3 \rightarrow OH+O_2$	1.16×10^{-11}
(R13)	$OH+O_3 \rightarrow HO_2+O_2$	1.11×10^{-14}
(R14)	$H+HO_2 \rightarrow 2OH$	7.20×10^{-11}
(R15)	$OH+OH \rightarrow H_2O+O$	1.18×10^{-13}
(R16)	$O_3+h\nu \rightarrow O_2+O$	1.00×10^{-2}

The rate coefficients of bimolecular reactions are given in units of $cm^3 s^{-1}$. The rate coefficients of termolecular reactions are calculated for conditions typical of the mesopause (concentration of air molecules (M)=1.7×10^{14} cm^{-3}, temperature t=189 K); the rate coefficients of (R6) and (R9) are given in units of s^{-1}, the rate coefficient of reaction (R11) is given in units of $cm^3 s^{-1}$. The photolysis rate coefficients (R7) and (R8) are given in units of $cm^{-3} s^{-1}$, and that of (R16) in units of s^{-1}.

2 The original and essential dynamic models of the mesospheric PCS: Description and basic dynamic properties

2.1 The original model of the mesospheric PCS

The detailed description of the model and its dynamic properties and characteristics can be found in FKM. Here we present a brief description of its essential features and a review of its dynamic properties and characteristics investigated in FKM.

A list of the photochemical reactions involved in the model, as well as their rates are given in Table 1. The reaction rates were calculated according to Atkinson et al. (1989) for the mesopause conditions, the altitude of approximately 82 km. The dynamics of the reagents involved in the model is described by a set of five ordinary differential equations (ODEs) for concentrations of the following reagents: O, H, O_3, OH, and HO_2. The model takes into account the diurnal variations of photolysis rates parameterized in the simplest form. Namely, we assume that the photolysis rates are constant during the daytime, jump to zero at sunset, and again jump to the daytime constant value at sunrise. Some remarks concerning validity of this assumption are given in FKM. Note that such an approximation of the diurnal variations of the photolysis rates allows us to reduce analysis of the behavior of a nonautonomous (time-dependent) system to analysis of

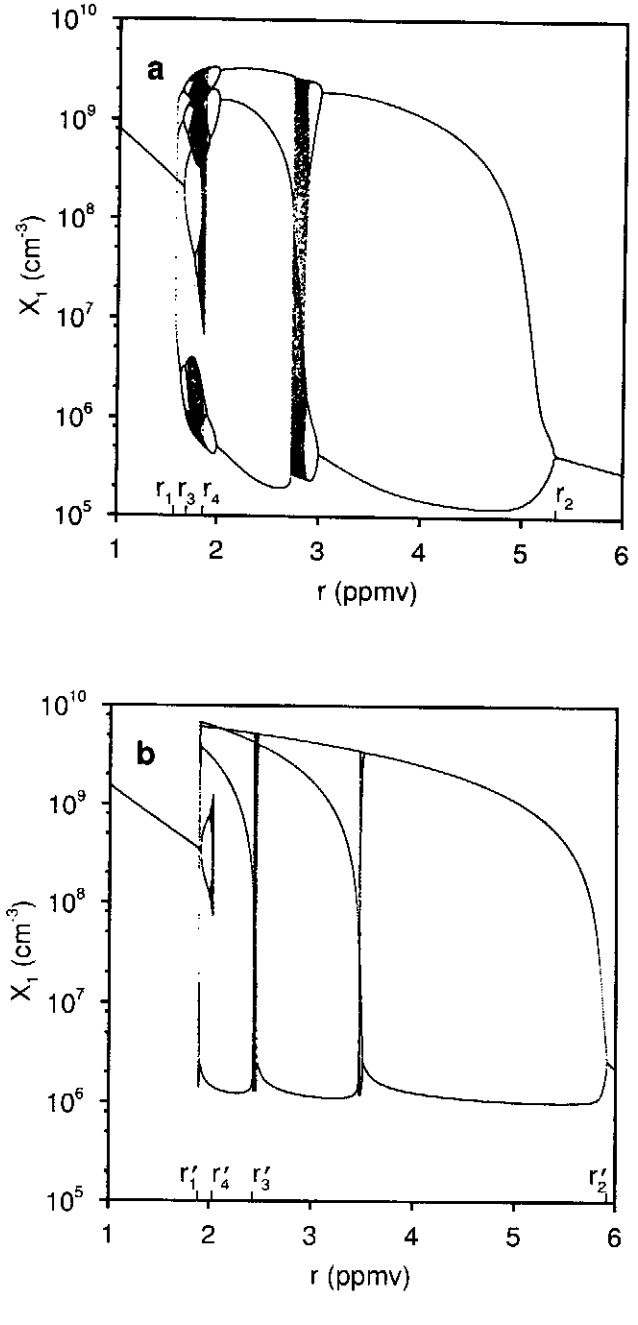

Fig. 1. Bifurcation diagrams for (a) the original and (b) essential dynamic models.

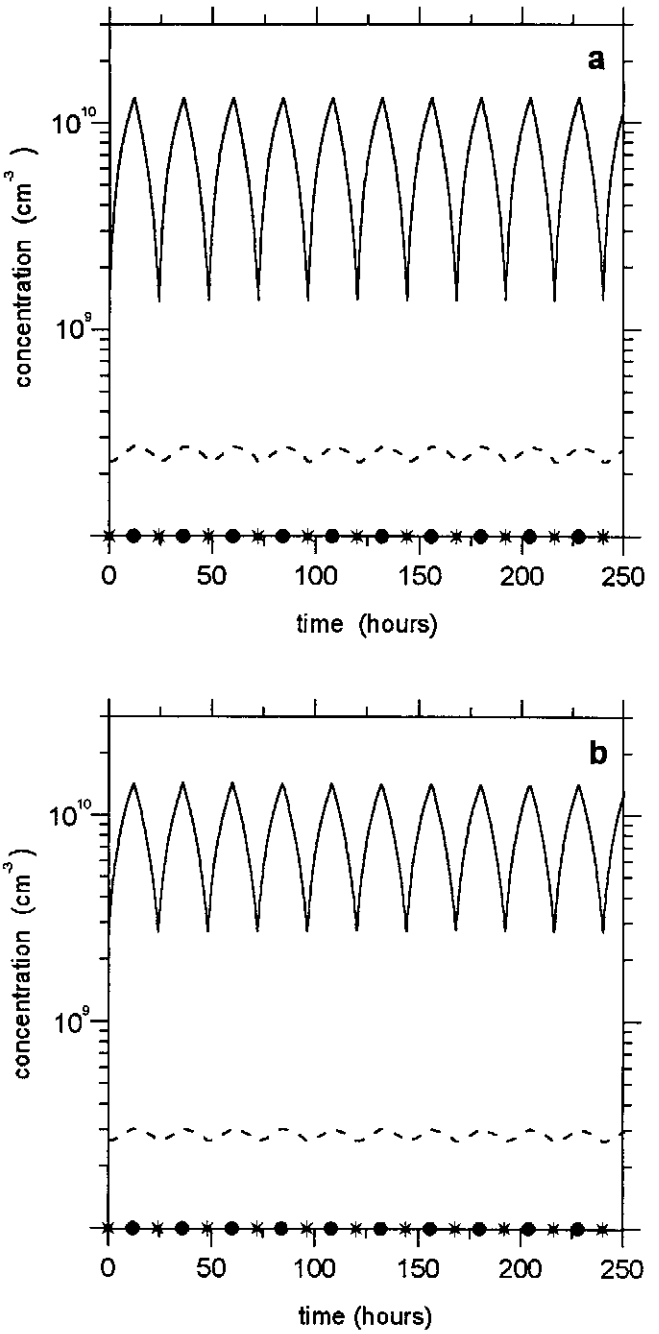

Fig. 2. Diurnal variations of the atomic oxygen (x_1) (solid line) and atomic hydrogen (x_2) (dashed line) in the one-day period regime with r=1 ppmv for (a) the original and (b) essential dynamic models. The asterisks and circles along the x-coordinate mark the moments corresponding to the sunrise and sunset, respectively.

that of two autonomous (time-independent) subsystems corresponding to daytime and nighttime conditions. Throughout this study, it is assumed for definiteness that duration of the day is equal to duration of the night.The original model possesses a rich assortment of possibilities of CDB (FKM). These possibilities are presented in the bifurcation diagram obtained in FKM and reproduced here in Fig. 1a. The diagram is formed by the atomic oxygen values (x_1) taken in the consecutive moments corresponding to the end of the night and separated by a 24-hours interval, that is, by a period of the parametric modulation. To obtain the diagram we made the sequence of calculations with both increasing and decreasing values of the water vapor mixing ratio denoted by r. Note that the latter is used as the control parameter throughout this study. As the initial values for the dynamic process with given r we use the night-end variable values found in the dynamic process with the previous value of r. The calculations are performed using a fifth-order Runge-Kutta method with a relative precision of 10^{-7} s. The diagram reflects, in particular, the presence of a double-periodic

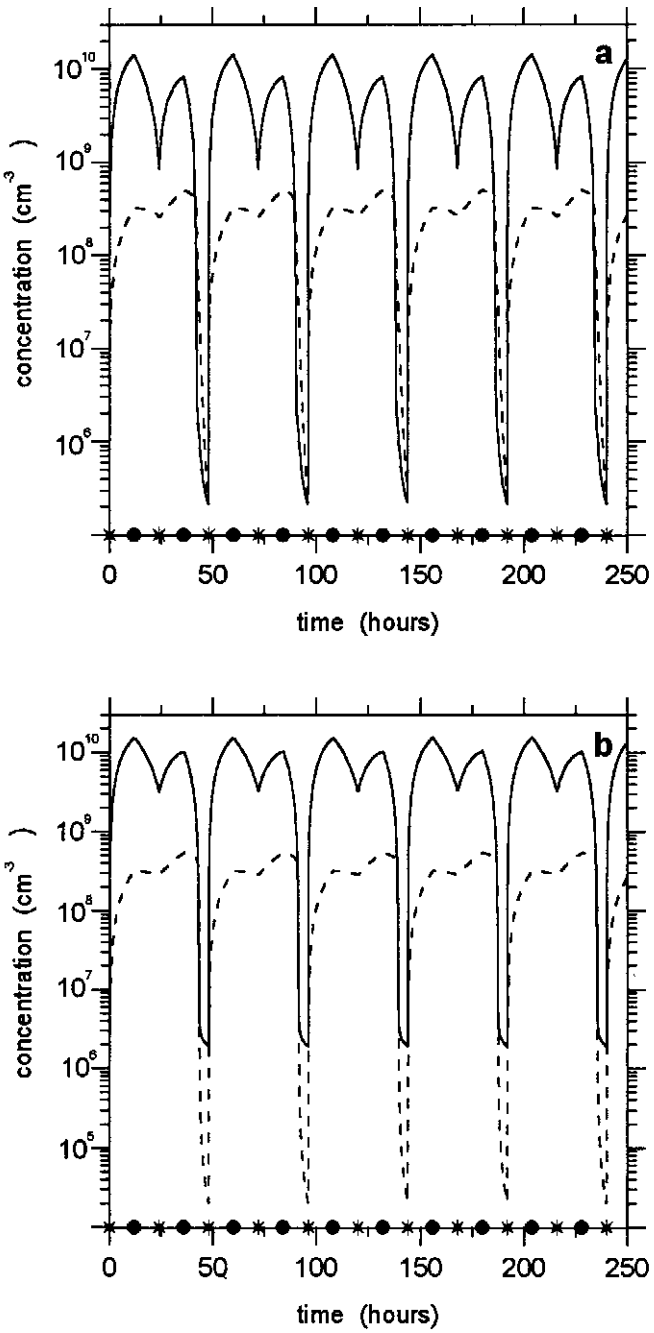

Fig. 3. The same as in Fig. 2, but for two-day period regime for r =4.3 ppmv.

regime, that is the regime with the minimal period of oscillations equal to two periods of parametric modulation (the bifurcation diagram is two-valued in the regions corresponding to this regime), triple-periodic, other multi-periodic, and chaotic regimes. The chaotic regimes correspond to the regions in the bifurcation diagram where, apparently, an infinite number of variable values are depicted for the same value of the control parameter. The region of CDB is bounded by the regions corresponding to the trivial one-periodic regimes. Figures 2a and 3a show examples of the diurnal variations of the atomic oxygen (solid line) and the atomic hydrogen (dashed line) in the one-periodic and double-periodic regimes, respectively. Note that the bifurcation diagram reflects the so-called hysteresis effect, when two different dynamic regimes are observed under the same value of the control parameter, depending on whether the control parameter value increases or decreases. We have also studied (see FKM) such dynamic characteristics as correlation and minimum embedding dimension of the chaotic attractor.

Investigations of the equilibrium state characteristics have shown (FKM) that the subsystem for the daytime evolution possesses a unique equilibrium state of the stable node-focus type, and the one for the nighttime evolution possesses that of the degenerate stable node type.

The knowledge of the mentioned characteristics was used in FKM for verification of the essential dynamic model described in Sect. 2.2.

2.2 The essential dynamic model of the mesospheric PCS

Following the special procedure of simplification proposed in FKM we obtained the essential dynamic model (EDM). The distinctive features of EDM are the following. It (1) involves only the "essence" of the chemical processes involved in the original dynamic model; (2) provides the simplest description of the dynamics of the chemical species; and (3) conserves the main qualitative dynamic properties and characteristics of the original dynamic model. The dynamics of EDM is described only by a set of two ODEs for concentrations of the atomic oxygen and the atomic hydrogen, which are denoted below by x_1 and x_2, respectively. Note that EDM actually involves only 9 chemical reactions from 16 in the original model. The EDM equations are the following:

$$\frac{d x_1}{dt} = -\alpha x_2 - (1-s(t))\mu x_1 + \delta s(t), \quad (1)$$

$$\frac{d x_2}{dt} = -\beta x_2^2/x_1^2 - \sigma x_2^2/x_1 + \gamma s(t) r, \quad (2)$$

where $\alpha=2a_6$, $\mu=a_9$, $\delta=2a_8$, $\beta=2a_3a_6^2/(a_5a_4)$, $\sigma=2a_6(a_1+a_2)/a_5$, $\gamma=2a_7$, and a_1-a_9 stand for reaction rate values of (R1)-(R9), respectively (see Table 1); r is a mixing ratio of the H_2O, $s(t)$ is a stepwise function modeling the diurnal variations of the photolysis rate values, that is determined as follows:

$s(t)=1$, $t\in[Tn;Tn+T/2]$, and $s(t)=0$,

$t\in[Tn+T/2;T(n+1)]$, $n=1,2...$ (3)

Concentrations of OH and HO_2 involved in the original model are determined as functions of x_1 and x_2 as follows:

$(OH)\approx a_6x_2/(a_4x_1)$, (4)

$(HO_2)\approx a_6x_2/(a_5x_1)$, (5)

$(O_3)\approx a_9x_1/a_{16}$ at daytime.

Concentration of O_3 at nighttime cannot be determined in the frameworks of the essential model, but its behavior is of no importance for evolution of dynamic variables of the essential model.

Figure 1b reproduces the bifurcation diagram for the EDM originally calculated in FKM. One can see, in particular, that as the value of the control parameter r decreases, both the original and essential models exhibit a cascade of period doublings leading to a chaotic regime, then there occurs a transition from the chaotic regime to the period-3 regime, and, further, to another chaotic regime through a cascade of period doublings. Note that the last cascade of period doubling is not resolved in Fig. 1b and an interested reader is referred to FKM where the first bifurcation in that cascade can be seen in the enlarged picture of the bifurcation diagram. However, as r decreases further, qualitative differences in the behavior of the original and essential models take place (see the region $r_1<r<r_3$ in Fig. 1a and the region $r_1'<r<r_3'$ in Fig. 1b). These differences that occur in rather narrow regions of the control parameter values are discussed in FKM. The causes of these differences are also discussed in detail in FKM. To put it briefly, any essential dynamic model, our mesospheric model included, that has been elaborated in accordance with the procedure described in FKM can be adequate to a source original model within but a limited region of the parameter values, and the changes of the essential model may be needed to make it adequate within other regions of parameter values. For the increasing values of r, both the original model (see the region $r_1<r<r_4$) and the essential model (see the region $r_1'<r<r_4'$) initially demonstrate a cascade of period doublings that lead to chaotic regimes. In this case, the only difference between the models is that the essential model possesses "a window" of the period-4 regime that divides the region of the chaotic behavior of the original model into two parts. Note that the regions of chaos and high-order subharmonics are much more narrow in the essential model than in the original one. However, we regard this difference between the models to be a quantitative one.

Figures 2b and 3b present examples of the diurnal variations of x_1 (solid line) and x_2 (dashed line) calculated in EDM in one-periodic and double-periodic regimes correspondingly (cf. Figs. 2a and 3a). The calculations of the correlation and minimum embedding dimensions of the chaotic attractor described by the EDM equations, as well as comparison of characteristics of the equilibrium state (see FKM), and evident qualitative similarity of the Poincare mappings of the original and essential models (see Sect. 3.2 and Figs. 9a and 9b in this paper) provide additional evidences of the qualitative similarity of the original and essential dynamic models.

We would like to emphasize that our study is focused on such "coarse" qualitative features of the original model as the presence of subharmonic and chaotic regimes and sequences of bifurcations causing transitions between them. Consequently, the simplified model is adequate to our task since it possesses essentially the same qualitative features as the original model. Any quantitative and the above-mentioned minor qualitative differences between the models are of no importance in the context of our task.

We believe that the comparison of the essential and original dynamic models indicates that the same factors are responsible for the origin of CDB in both the original model and the EDM. Thus, we have grounds to employ the EDM as a tool for revealing the origin of CDB of the original model. The corresponding analysis is described in the sections to follow.

3 Peculiarities of the one-day evolution of the system responsible for CDB during multi-day evolution. Mechanisms of originating CDB

As follows from the preceding consideration, CDB of the mesospheric PCS can be manifested in a dynamic process lasting for several days at least. However, it seems reasonable to assume that the existence of CDB in such a dynamic process is predetermined by some peculiarities of the one-day evolution. In this section we reveal and analyze both these peculiarities and the mechanisms conditioning their essential role. Toward this end, we use independently two approaches to qualitative analysis of a dynamic system, traditional in nonlinear dynamics, that are described in Sects. 3.1 and 3.2, respectively. Each of the approaches provides unique information about the processes determining EDM behavior and allows us to create a physically illustrative image for CDB mechanisms.

3.1 Analysis of the factors responsible for the dynamics of infinitesimal perturbations of a solution of the set of Eqs. (1)-(3)

The principal nonlinear effects demonstrated by the mesospheric PCS are (Sonnemann and Fichtelmann, 1997; Feigin et al., 1998) (1) the bifurcations associated with stepwise changes of a minimum period of the solution, and (2) the chaotic regimes. A bifurcation associated with a sudden appearance of period-n solution instead of period-m solution is a result of an instability of period-m solution corresponding to an exponential growth with time of any infinitesimal perturbations of the unstable solution. If there are no stable solutions, we have a chaotic solution. Thus, the exponential (on the average) growth with time of an arbitrary infinitesimal perturbation of an arbitrary solution of the system is a property and both the sufficient and necessary conditions of the chaotic regime. To put it differently, a positiveness of the Lyapunov indexes is both the property and the criterion of the chaotic solution (see, for example, Moon, 1987). For these reasons, to fulfill our task we analyze, first of all, the factors determining dynamics of the infinitesimal perturbations of the chaotic solution of the system and the mechanisms of the growth of these perturbations. In doing so we assume that the same factors determine the growth of the unstable subharmonic solutions. We analyze such factors in two independent ways. First, we consider the equations describing dynamics of infinitesimal perturbations and their solutions (see Sect. 3.1.1), and then we analyze the behavior of a pair of close phase trajectories in the phase space of the subsystems

corresponding to daytime and nighttime conditions (see Sect. 3.1.2).

3.1.1 Analysis of the equations for infinitesimal perturbations of solution

Let us consider two different solutions ($x_1(t)$, $x_2(t)$) and ($x_1'(t)$, $x_2'(t)$) of the set (1)-(3), such that $|x_{1,2}'-x_{1,2}| \ll |x_{1,2}|$. Linearizing Eqs. (1)-(2) we obtain the following set for infinitesimal perturbations $\xi_{1,2}=x_{1,2}'-x_{1,2}$ of the solutions.

$$\frac{d\xi_1}{dt} = -\alpha\,\xi_2 - (1-s(t))\mu\,\xi_1, \qquad (6)$$

$$\frac{d\,\xi_2}{dt} = A\,\xi_1 - B\,\xi_2, \qquad (7)$$

where $A = \frac{x_2^2}{x_1^2}\left(\frac{2\beta}{x_1}+\sigma\right)$, $B = \frac{2\,x_2}{x_1}\left(\frac{\beta}{x_1}+\sigma\right)$.

Replacing $\xi_{1,2}$ in Eqs. (6)-(7) by $\xi_{1,2}=\bar{\xi}_{1,2}\exp\left(\int (s(t)-1)\mu dt\right)$ and making evident rearrangements we obtain the following equation:

$$\frac{d^2\bar{\xi}_1}{dt^2} + 2\nu(t)\frac{d\,\bar{\xi}_1}{dt} + \omega_0^2(t)\,\bar{\xi}_1 = 0, \qquad (8)$$

where $\nu(t)=(B+(s(t)-1)\mu)/2$, $\omega_0^2(t)=\alpha A$.

The structure of this equation is identical to that of the equation describing a linear oscillator with time-dependent friction (ν) and eigen-frequency (ω_0). The chaotic and multi-periodic regimes are associated with the increase of ξ_1, and thus, $\bar{\xi}_1$ with time. Note that the "frequency" ω_0 is always positive as in the case of a real physical oscillator. The "friction" ν can be either positive or negative; it may be negative exclusively due to $\mu\neq 0$. However, it is clearly seen from (6) that the only role of the term proportional to μ consists in damping perturbation ξ_1 during the nighttime evolution. Indeed, our numerical experiments have shown that, while $\mu=0$, the system, in spite of the changes that make its behavior even more complicated, retains all the types of CDB of EDM. We would like to emphasize that negative dissipation does not actually exist in the set (6), (7), and negativeness of friction in (8) is just a consequence of the replacement of variables. Thus, we can conclude that possible negativeness of ν is not a factor responsible for the growth of ξ_1. It is also easy to prove rigorously that an arbitrary modulation of the friction which holds it positive (this is always fulfilled in our model in the case $\mu=0$) cannot cause the growth of ξ_1. Hence, the above consideration shows that we deal with parametric excitation of the oscillator (8) due to time-dependence of its eigen-frequency ω_0. Consequently, the peculiarities of the process of parametric excitation are determined by the peculiarities of time dependence ω_0. This dependence calculated for the chaotic regime (r=2.442 ppmv) is presented in Fig. 4a.

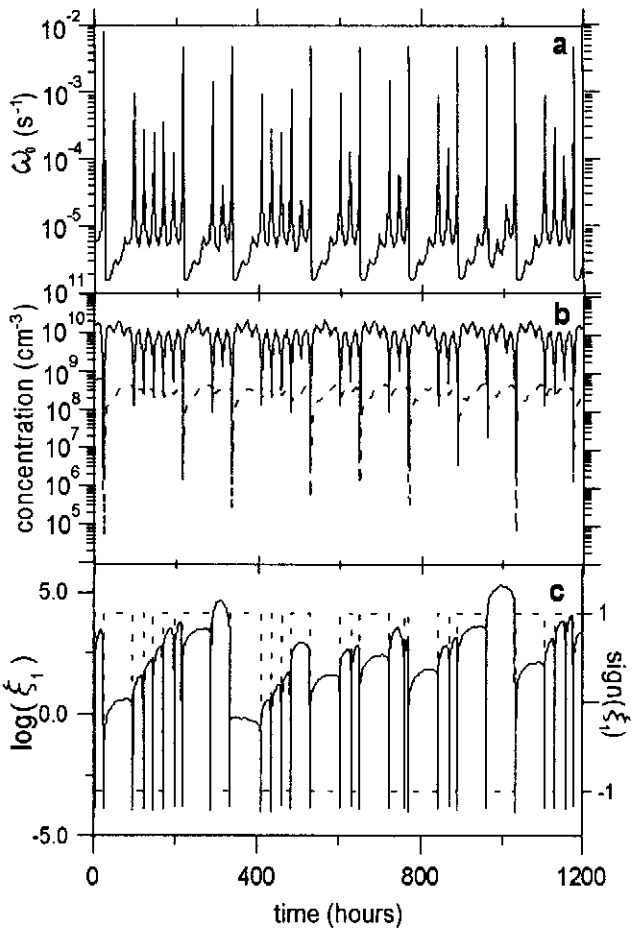

Fig. 4. Time dependences of (a) the frequency (ω_0) of the linear oscillator (8), (b) concentrations of atomic oxygen, x_1 (solid line), and atomic hydrogen, x_2 (dashed line), and (c) logarithm of the magnitude (solid line) and sign (dashed line) of the perturbation ξ_1. The dependences have been calculated in the essential dynamic model for r=2.442 ppmv.

An apparent feature of this dependence is a sequence of extremely strong pulses (note that the scale of the ordinate is logarithmic). Figure 4b illustrates the corresponding chaotic oscillations of x_1 and x_2. Comparison of Figs. 4a and 4b shows that the pulses of ω_0 are associated with abrupt and deep "drops" of the variables at the end of the nighttime evolution. Figure 4c presents the corresponding oscillations of ξ_1. The logarithm of the absolute value of ξ_1 is shown by a solid line, and the sign of ξ_1 (reflected as either plus or minus unity) is shown by a dashed line. Several segments of the exponential growth of the amplitude of ξ_1 can be seen in Fig. 4c. According to Fig. 4a, the dependence of ω_0 on time in these segments can be roughly approximated as a periodic sequence of δ-pulses, that is

$$\omega_0^2 = a\sum_n \delta(t-nT), \; n=1,2..., \qquad (9)$$

where T is a time period between δ-pulses. Note that Eq. (8), when $\nu=0$ and ω_0^2 is an arbitrary periodic function, is known as the Hill equation. This equation is known to

possess exponentially growing solutions. Analytical handling of the Hill equation with ω_0^2 defined according to (9) shows that the solution grows with time, whenever $aT>4$. A minimum period of the unstable oscillations therewith equals $2T$, as in the cases reflected in Fig. 4. An increment of the oscillations described by such an equation increases with an increase of pulse amplitude a. Note that when the discussed Hill equation contains an additional term describing friction and proportional to $\nu\neq 0$, the pulse amplitude needed for excitation of unstable oscillations is much greater than in the "ideal" case $\nu=0$. This explains the necessity of very strong pulses of ω_0 in the case of Eq. (8) because of strong dissipation inherent in the set (6), (7), and in EDM itself.

The facts pointed above bear witness to the essential role of δ-wise pulses of ω_0 in the processes of excitation of exponentially (on the average) growing oscillations of the small perturbations $\xi_{1,2}$ described by (8), and thus in the processes causing CDB. Since the pulses of ω_0 are associated with deep night drops of variables, the results obtained demonstrate the essential role of these drops. Numerical experiments show that the presence of the strong pulses of ω_0 associated with night drops is characteristic for all types of CDB of EDM. However, excepting chaotic solutions, $\xi_{1,2}$ are everywhere damping. Note that $\xi_{1,2}$ would be growing also in the case of unstable solutions but we could not obtain unstable solutions by means of numerical integration of the evolutionary equations.

Note also that one of the results of the above analysis is demonstration of a physically illustrative mechanism of originating CDB: CDB appears as a result of specific parametric instability of small perturbations of the solution of the EDM equations.

3.1.2 Analysis of phase space

An imaginary space whose coordinates are the system variables is referred to as the phase space of the system. An analysis of the phase space is a traditional and very useful tool for investigations of qualitative dynamic properties of a dynamic system. Any solution of the system is reflected in the phase space by means of a phase trajectory. The point of the phase space corresponding to the instantaneous state of the system and tracing out a certain phase trajectory during the evolution of the system is referred to below as an imaging point (IP). Of special interest for us is mutual behavior of a pair of initially closely-spaced phase trajectories. Obviously, an increase or a decrease of the distance between the IPs belonging to these trajectories corresponds unambiguously to the growth or damping of small perturbations of the solution, respectively. In this section, we analyze dynamics of the distance between such IPs.

Let us mention two ways for presentation of the phase space of the system described by Eqs. (1)-(3).

1. Note that our nonautonomous (time dependent) system can be transformed into the autonomous one owing to periodic dependence of its parameters on time. For this an additional differential equation for cyclic variable should be written (see, for example, *Moon*, 1987). The phase space of the obtained autonomous system appears as three-dimensional space "rolled up" along the cyclic coordinate.

2. The other way is based on the fact that, due to the stepwise dependence of the photolysis rates on time, the dynamic process described by Eqs. (1)-(3) can be represented as a sequence of dynamic processes described by the autonomous systems corresponding to the daytime

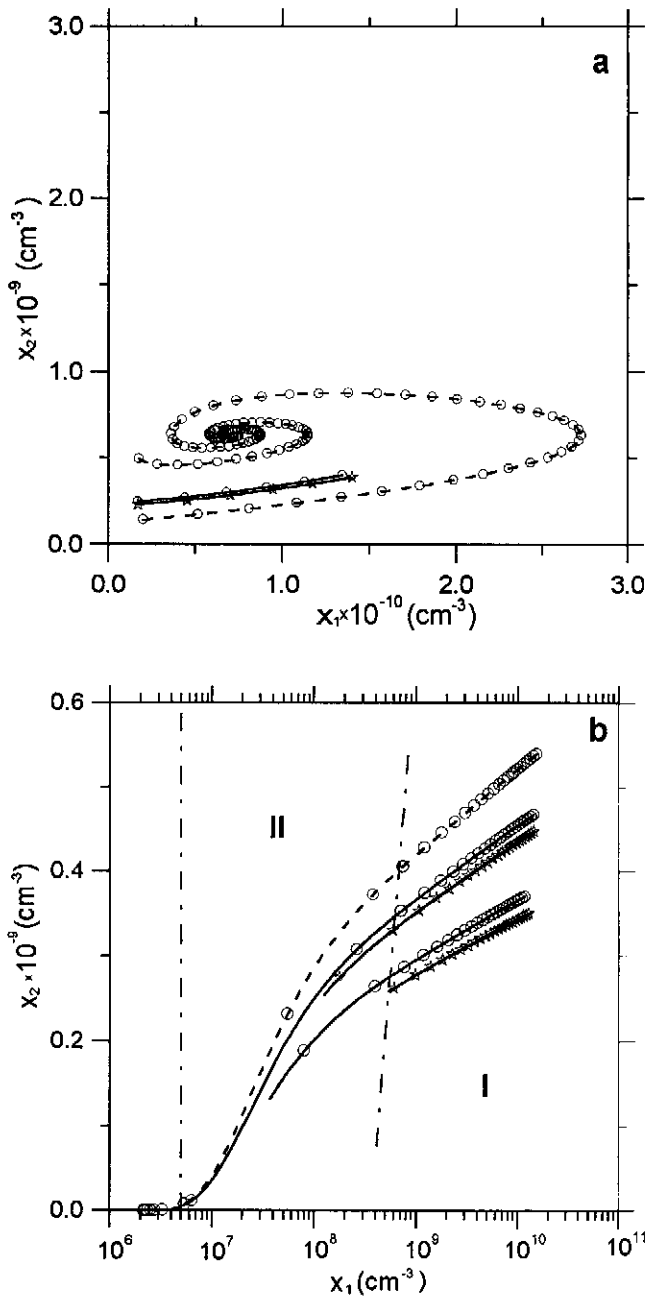

Fig. 5. Several phase trajectories in the phase space of the set (1)-(2) (for r=2.442 ppmv) for the daytime (a) and nighttime (b) conditions. The dashed lines correspond to the arbitrary chosen trajectories exhibiting the characteristic qualitative features of the phase spaces structure. The solid lines with asterisks depict some pieces of phase trajectories observed in the chaotic regime, corresponding to either daytime or the nighttime evolution, and those with circles show pieces of neighboring trajectories.

and nighttime situations. Hence, to analyze the evolution of the nonautonomous system, we should consider two phase spaces reflecting daytime and nighttime situations. An IP spends a fixed time inside one phase space, and, after that, passes into another. Note that the phase trajectory is not disrupted as it passes "the boundary" between the daytime and nighttime phase spaces.

In this study we use the second way. Characteristic features of the structure of the phase spaces corresponding to the daytime and nighttime conditions are shown in Figs. 5a and 5b, respectively, by some phase trajectories depicted by the dashed line. The "velocity" of IP motion in the phase space can be judged by stroboscopic marks on the trajectories. The mentioned trajectories illustrate, primarily, the fact that the structure of each of the phase spaces is determined by a single attractor (see also FKM). Indeed, all the phase trajectories in the daytime phase space come to the equilibrium state of the stable focus type, and those in the nighttime phase space converge to the singular equilibrium state at the origin of the phase space coordinates.

The solid lines with asterisks represent some arbitrary chosen trajectories observed in the chaotic regime and corresponding to either daytime or nighttime evolution, and those marked by circles show arbitrary neighboring trajectories: duration of motion along these pieces of phase trajectories is also equal to duration either of day or night. Note that the closely spaced trajectories do not diverge, in geometrical sense, in either of the considered phase spaces of our system, unlike the case of phase spaces of many chaotic subsystems (e.g., the Rossler equations (Rossler, 1976)). However, as can be seen from Figs. 5a and 5b, the distance between the IPs on the neighboring trajectories can increase both in daytime and nighttime phase spaces despite the absence of divergence. From the figures we notice that the increase of the distance between the initially close IPs is possible owing to two following conditions. (1) The closely-spaced trajectories do not converge significantly during considered stages of the evolution, and (2) the velocities of the IP motion are different along different trajectories. The first condition determines the obvious restriction on the duration of the considered stages of evolution under chaotic behavior of the system: the imaging point must not have time enough to reach the equilibrium during the evolution. Factors responsible for the fulfillment of the condition (2) are analyzed in Sect. 4. Note that divergence, in geometrical sense, of phase trajectories is also absent in the phase of the well-known Lorenz equations (Lorenz, 1983). However, the mechanism of CDB appearance in the Lorenz's system (see, e.g., Williams, 1977) differs from those discussed below.

Note that the distance between the neighboring IPs grows in different ways during different stages of the evolution. During the daytime evolution, the difference between the values of x_2 coordinates of two IPs leads to an increased difference in x_1 but the difference in x_2 does not increase. The nighttime evolution can be divided into two distinctive successive stages associated with different ways of increasing distance between neighboring IPs. The domains of these stages are roughly reflected in Fig. 5b. The process of the growth of the distance during the first stage is the same as during the daytime evolution. The second stage is characterized by an abrupt increase of the velocity of the IP motion, and, namely this stage is associated with the nighttime drops of the variable values, noted in the previous section. Beginning at different moments for different phase trajectories, this stage causes a significant increase of the distance between the neighboring IPs along the x_2-coordinate. Note also that this stage is associated with "turning over" of the length connecting two neighboring IPs. As a result of this turning over, trajectories with initially greater x_2 have smaller x_2 at the end of the stage, and vice versa. The turning over reflects the oscillating character of the behavior of small perturbations, which has been revealed in the previous section. The second stage is followed by an abrupt decrease of the velocity of IP motion and, consequently, by a decrease of the distance between the neighboring IPs.

To conclude this section, let us summarize the description of the revealed mechanism responsible for an increase of the distance between the neighboring IPs. During the daytime, and the first stage of the nighttime evolution, the difference in the x_2-coordinate of IPs causes the difference in x_1. During the second stage of the nighttime evolution, the difference in x_1 transforms again to the difference in x_2 which is larger than the initial one. The fact that the initial difference in the x_2-coordinate of IPs transforms back into the larger difference in x_2 during the consequent daytime and nighttime evolution reflects the possibility of exponential growth of the distance between IPs during the multi-day evolution. We see that the growth of the distance along x_2 takes place only during the second stage of the nighttime evolution, so this is an evidence of the major importance of that stage in the processes responsible for the appearance of NDB. This conclusion is in complete accordance with the results of the previous section. At the same time, we can assume that the increase of the distance between IPs along x_1 during the daytime evolution is not necessary for CDB because this process is duplicated during the first stage of the nighttime evolution. The validity of this assumption is corroborated by results of Sect. 3.2.

3.2 Analysis of the Poincaré mapping

One of the most effective methods for studying periodically repeated processes is the method of Poincaré mappings. It consists in reducing the analysis of the evolutionary differential equations to the analysis of the mapping connecting the variable values separated by a characteristic time interval. In this way, the evolution of our system can be represented by means of the 2d mapping of the following form:

$$x_{1,2}^{n+1} = f_{1,2}\left(x_1^n, x_2^n\right) + g_{1,2}\left(f_{1,2}\left(x_1^n, x_2^n\right), f_{1,2}\left(x_1^n, x_2^n\right)\right), \quad (10)$$

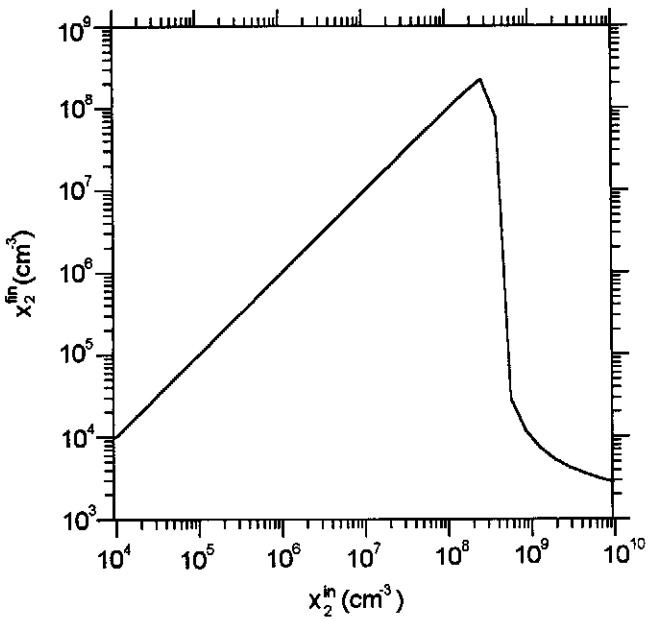

Fig. 6. Nighttime evolution mapping (NEM), that is, the dependence of the atomic hydrogen concentrations at the end of the night on the ones at the beginning of the night.

where $x_{1,2}^n$ are variable values at the instant the night stage begins, and $x_{1,2}^{n+1}$ are variable values after the period of external modulation. Functions $f_{1,2}$ give variable values after the nighttime evolution, and functions $g_{1,2}$ describe changes of variable values after the daytime evolution. These functions are uniquely determined by Eqs. (1)-(3) but cannot be described analytically. The geometric image of the mapping (10) is a surface in the 4-dimensional space whose coordinates are $x_{1,2}^n$, $x_{1,2}^{n+1}$. Thus, the mapping (10) is not yet a convenient object for qualitative analysis.

Below we demonstrate that the essential features of the dynamic behavior of the system (1)-(3), such as the presence of subharmonic and chaotic oscillations, and the specific sequence of the bifurcations described in Sect. 2, can be represented by means of a significantly simpler 1d mapping. For this we use the results of Sects. 3.1.1 and 3.1.2 which show that the mechanisms of CDB origination are associated mainly with the nighttime evolution, especially, with the behavior of x_2 during this stage. Thus, before proceeding further, we consider separately the dependence of function f_2 on x_2. In other words, we consider the dependence of the x_2 value at the end of the nighttime evolution on that at the beginning. Hereinafter we refer to this dependence as to the nighttime evolution mapping (NEM). Figure 6 presents the NEM calculated for initial concentration $x_1=10^{10}$ cm^{-3}.

The shape of the NEM obtained reflects the presence of different stages of the nighttime evolution defined in Sect. 3.1. Specifically, the growing portion of the NEM appears because the nighttime evolution with relatively small initial values of x_2 corresponds to the first stage only.

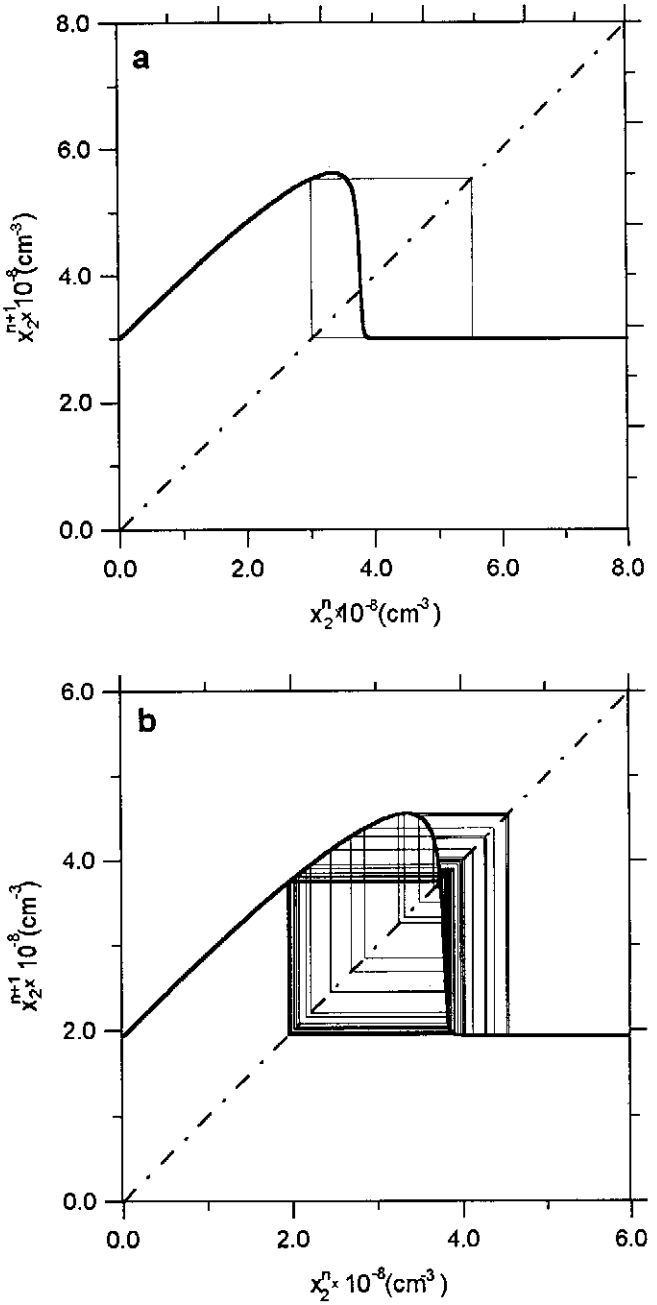

Fig. 7. The 1-d mappings (thick solid line) calculated according to equation (13) for the parameter values corresponding to (a) the period-2 (r=4.5 ppmv), and (b) the chaotic regimes (r=2.86 ppmv). The structures of the corresponding solutions are shown by the thin solid line.

In other words, NEM increases when the duration of the first stage (τ_d) is greater than the duration of the night itself. It is shown in Appendix (see (A4)) that τ_d is inversely proportional to the initial x_2 value. Hence, with an increase of the latter, τ_d can become equal to the duration of the night. A further increase of the initial value of x_2 would be associated with an abrupt decrease of the final x_2 value during the second stage of the nighttime evolution. This fact is reflected in NEM as a strong bend. The following slowly decreasing portion of NEM corresponds to the stage

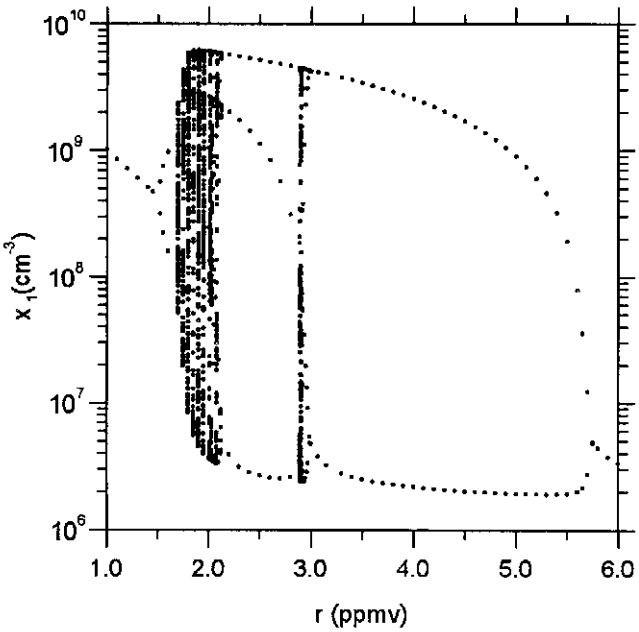

Fig. 8. The bifurcation diagram calculated in accordance with the 1-d mapping (13). For ease of comparison with the bifurcation diagrams of the original and essential models (Figs. 1a and 1b) this diagram depicts the value of x_1 which is the single valued function of x_2 involved in (13).

of slow adjustment of the system to the nighttime equilibrium state.

Although NEM is just part of the mapping reflecting the total evolution of the system, it is useful to note that it possesses a "one-hump" structure characteristic of the family of mappings considered by Feigenbaum (1978), and, specifically, for the famous logistic map. He demonstrated that such mappings can possess a period doubling cascade. Note also that the most general feature of these mappings is that they are irreversible: one final value can correspond to two initial values. The noted qualitative resemblance of NEM to Feigenbaum mappings and comparatively smooth daytime evolution of the system (see Sects. 3.1.2 and Fig. 5a) allow us to assume that possibility of CDB in our system is connected, above all else, with the specific form of the obtained NEM. To prove this assumption we make the simplest approximation of the daytime evolution. Based on results of our numerical investigation of the set (1)-(3) we suppose (1) that x_2 increases by a fixed constant value proportional to r during the daytime evolution, and (2) that the x_1 value final for the daytime evolution is a fixed constant independent of initial conditions of the daytime evolution. That is, we assume the functions g_1 and g_2 to be of the form

$$g_1 = C_1 - f_1\left(x_1^n, x_2^n\right), \tag{11}$$

$$g_2 = C_2 r = const, \tag{12}$$

where C_1 and C_2 are constants.

Substituting (11) and (12) into (10) we obtain the following 1d mapping:

$$x_2^{n+1} = f_2\left(x_2^n, C_1\right) + C_2 r \tag{13}$$

which is much simpler. This mapping calculated for $C_1=10^{10}$ cm^{-3}, $C_2=6.7\times10^{7}$ cm^{-3} and r=4.5 ppmv is depicted in Fig. 7a by a thick solid line. Note that similarly to the Feigenbaum mappings, the mapping (13) has a one-hump structure and, consequently, can describe, depending on parameter values, a number of multi-periodic regimes. For example, Fig. 7a shows the structure of the period-2 solution of the mapping (13). Figure 7b presents the mapping corresponding to the chaotic regime. It has been calculated for the above noted values of C_1 and C_2 but for r=2.89 ppmv. A piece of the chaotic solution is also shown. The last mapping allows us to illustrate the growth of the perturbations of an arbitrary solution. Indeed, let us suppose that the initial values of x_2 correspond to the region of the strong bend of the mapping. Then, it is easy to perceive that an arbitrary small perturbation of this initial value of x_2 increases significantly after iteration. Reiterations would result in exponential (on the average) growth of the perturbations, that is, in chaotic behavior.

Figure 8 presents a bifurcation diagram for the mapping (13). For ease of comparison with the bifurcation diagrams of the original and essential models calculated earlier (see Figs. 1a and 1b), we give in the diagram the night-end values of x_1, but not of x_2, as would be in accordance with (13). The night-end values of x_1 are obtained immediately in the same calculations using Eqs. (1), (2), as x_2. Comparison of the noted bifurcation diagrams bears witness that the mapping (13) retains such essential features of the behavior of both the original and essential models as the presence of the period doubling cascade completed by the chaotic regime, and the presence of the wide region of the period-3 solution at the other side of the chaotic band. Moreover, even certain quantitative correspondence of the diagrams presented both in Figs. 1a, b and Fig. 8 occurs. The major qualitative difference is observed under relatively small values of the control parameter r: it is seen that the mapping (13) can describe more complex behavior than both the essential and original model. This difference means that our assumptions used for the derivation of (13) are not valid for this region of r values. Note that the behavior of the essential model also differs from that of the original model under small values of r (see Sect. 2, or extended discussion in FKM).

For completeness, it is useful to understand the relationships between the simplified 1d mapping (13), 2d mapping (10) for the essential model, and the analogous 5d mapping for the original model. For this purpose, let us consider the images of the chaotic attractors in the space of the above noted mappings. Since the 1d mapping (13) is formulated in terms of the x_2 values, it is natural, in the case of the essential and original models, to consider projections of the attractor images onto the (x_2^n, x_2^{n+1}) plane too. Figures 9a - 9c present such images corresponding to the rightmost chaotic bands in the bifurcation diagrams (see Figs. 8, 1b, and 1a, respectively).

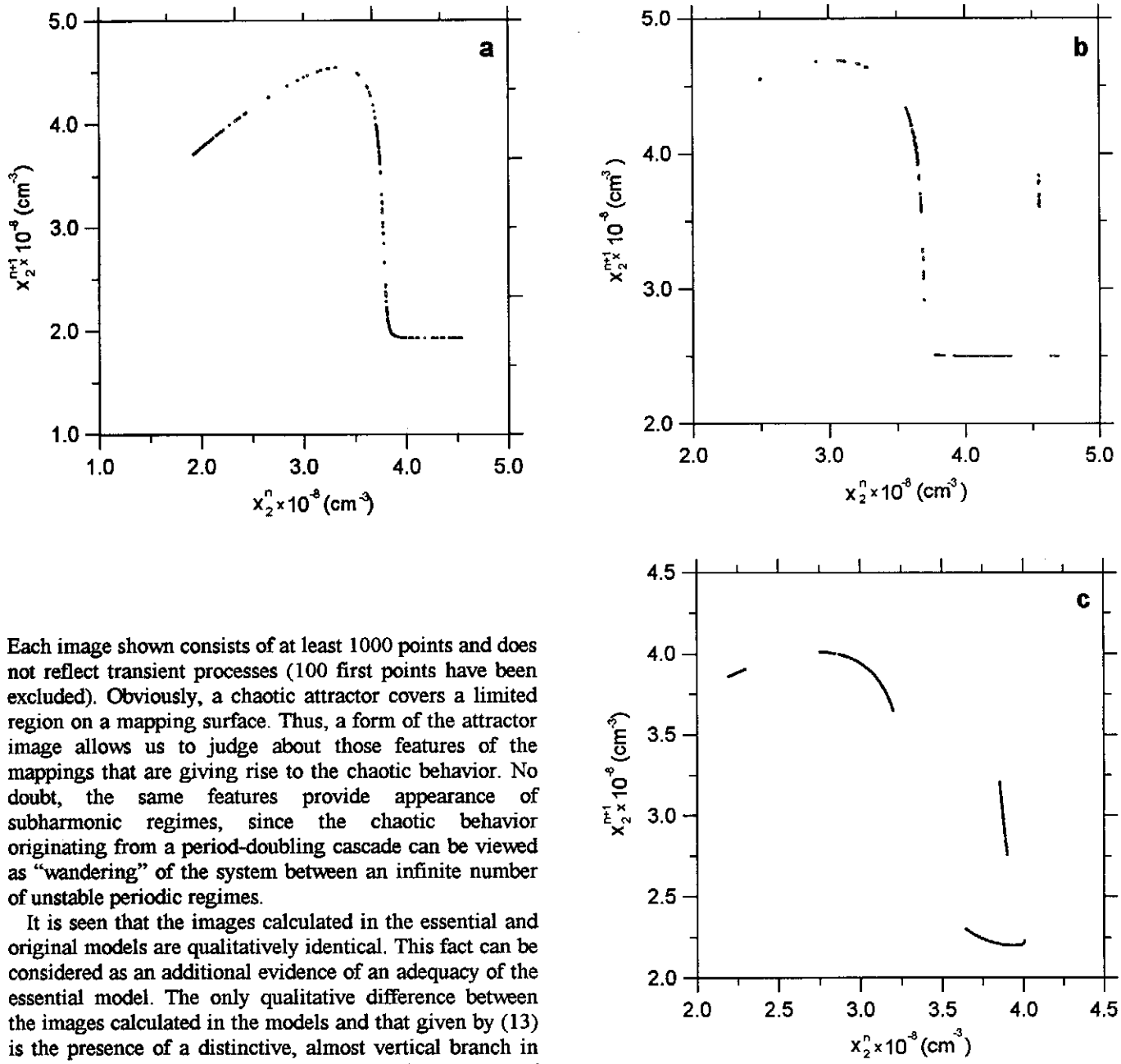

Fig. 9. The images of a chaotic attractor at the map (x_2^n, x_2^{n+1}), where x_2^n is concentration of atomic hydrogen at the end of the daytime of the n-th day of evolution calculated by means of (a) 1d mapping (13), (b) the essential dynamic model (r=3.475 ppmv), and (c) the original dynamic model (r=2.86 ppmv).

Each image shown consists of at least 1000 points and does not reflect transient processes (100 first points have been excluded). Obviously, a chaotic attractor covers a limited region on a mapping surface. Thus, a form of the attractor image allows us to judge about those features of the mappings that are giving rise to the chaotic behavior. No doubt, the same features provide appearance of subharmonic regimes, since the chaotic behavior originating from a period-doubling cascade can be viewed as "wandering" of the system between an infinite number of unstable periodic regimes.

It is seen that the images calculated in the essential and original models are qualitatively identical. This fact can be considered as an additional evidence of an adequacy of the essential model. The only qualitative difference between the images calculated in the models and that given by (13) is the presence of a distinctive, almost vertical branch in the right-hand parts of Figs. 9b and 9c. The presence of this branch bears evidence that the mappings of the essential and original models are not really 1-dimensional, and that the structures of the chaotic and periodic solutions described, on the one hand, by the 1d mapping, and, on the other hand, by the essential or original model are somewhat different. However, comparison of the bifurcation diagrams (see above) allows us to argue that, when the existence of the main regimes of CDB (period-2, period-3, and chaotic regimes) in the mesospheric photochemical system is of primary interest, the noted difference is of minor significance, and that the mechanism of CDB origination in this system, when 1d mapping adequately reproduces qualitative features of the behavior of the models, is essentially the same as that described by Feigenbaum.

To conclude section 3 let us summarize the main peculiarities in the behavior of the system during one period of parametric modulation, which give rise to the CDB. These are the following:

(i) the stage of abrupt changes of variable values during nighttime evolution, and

(ii) the "humped" structure of the nighttime evolution mapping for x_2.

4 Peculiarities of the modeled chemical processes

The main objective of this section is determination of the peculiarities of the modeled chemical processes which condition the appearance of CDB. To achieve this goal we first analyse the dynamic equations and determine the terms responsible for the characteristic features of the behavior of the system during various stages of the diurnal evolution (Sect. 4.1), and, second, we determine the peculiarities of chemical processes described by these terms (Sect. 4.2).

4.1 Analysis of the dynamic equation structure

4.1.1. The daytime and first stage of the nighttime evolution. Both these stages (see Sect. 3.1.2 for definitions and description of the stages of the diurnal evolution) are characterized by significant relative changes of x_1 and much smaller ones of x_2. Thus, while considering the peculiarities of the system evolution during a single period of modulation, it seems to be quite valid to neglect changes of x_2. In other words, the changes of the variable values during these stages can be described approximately only by Eq. (1) under the supposition x_2=const. (Note that such an assumption is invalid while analyzing regularities of the multi-period evolution, as in the previous section.) Keeping in mind this approximation it is easy to see the reasons for increasing the distance between the IPs of two closely-spaced trajectories along the x_1-coordinate. Indeed, let us consider two closely-spaced phase trajectories which initially have equal values of x_1 but different values of x_2 (see Fig. 5a, the solid lines with circles and asterisks). Then, due to the term "$-\alpha x_2$" of (1), the x_1 value at the end of the daytime evolution will be greater for the trajectory with smaller initial value of x_2 and vice versa. Although Eq. (1) for the nighttime differs from that for the daytime, the changes of the distance between the IPs during the first stage of the nighttime evolution are again determined by the term "$-\alpha x_2$". Obviously, the role of the term "$-\mu x_1$" is opposite to the role of the term "$-\alpha x_2$".

4.1.2. The second stage of the nighttime evolution. The peculiarities of the system behavior during the second stage of the nighttime evolution characterized by the abrupt changes of variable values can be explained as follows. First note that this stage begins after the significant decrease of x_1 during the previous stage of the nighttime evolution. For this reason we can neglect the term "$-\mu x_1$" in the following consideration. As long as a relative rate of changes of x_2 (that is, $x_2^{-1}\left|dx_2/dt\right|$) is negligible compared with that of x_1, the absolute rate of a decrease of x_1 remains approximately constant with time, and the relative rate grows almost hyperbolically. However, such a decrease of x_1 (that is, concentration of atomic oxygen) cannot last infinitely because the concentration of a chemical reagent is always a nonnegative number. Slowing down of dropping of x_1 is possible and indeed takes place due to a decrease of the x_2 value. This decrease takes place due to the terms "$-\beta x_2^2/x_1^2$" and "$-\sigma x_2^2/x_1$" of (2). As follows from results of Sect. 3.1.2 (see Fig. 5b), the decrease of x_2 leads eventually to a drop of both the absolute and relative rates of changes of x_1.

Let us show first that significant slowing down of the relative rate of changes of x_1 occurs as a result of significant acceleration of the relative rate of changes of x_2. Indeed, the instant of cessation of further growing of the x_1 relative rate, in other words, its maximum is, obviously, determined by the condition

$$\frac{d}{dt}\left(\frac{1}{x_1}\frac{dx_1}{dt}\right)=0. \tag{14}$$

Substituting Eq. (1) (for μ=0) into (14), we find that (14) is equivalent to the condition that the relative rates of changes of x_1 and x_2 are equal:

$$\frac{1}{x_1}\left|\frac{dx_1}{dt}\right|=\frac{1}{x_2}\left|\frac{dx_2}{dt}\right|. \tag{15}$$

Clearly, for initially significantly unequal rates of variable changes to become equal, the more rapid growth of the rate of changes of x_2 is needed as compared to that of x_1.

Let us demonstrate now that this more rapid growth is possible due to the presence of the term "$-\beta x_2^2/x_1^2$" in Eq. (2), or, to be more specific, due to the fact that this term is inversely proportional to x_1^2. Indeed, assuming β=0, we see that

$$\frac{1}{x_1}\left|\frac{dx_1}{dt}\right|=\frac{\alpha x_2}{x_1}=\frac{\alpha}{\sigma x_2}\left|\frac{dx_2}{dt}\right|. \tag{16}$$

That is, we see that, if Eq. (2) did not contain the term "$-\beta x_2^2/x_1^2$", the relative rates of changes of x_1 and x_2 would be proportional during the whole nighttime evolution, and could not become equal. As a result, the relative rate of changes of x_1 would never reach its maximum (see (14) and (15)) and approach infinity when x_1 tends to zero. This means that, eventually, x_1 would inevitably become negative. It is needless to say that because of such a behavior the model with β=0 is inadequate. So, we may indeed conclude that the term "$-\beta x_2^2/x_1^2$" is of particular importance for the nighttime evolution of x_2. Note that the exact solution of the system (1), (2) with $\beta=\mu=s=0$ can be easily obtained analytically, but it will not be discussed here. Naturally, the exact solution corroborates the above qualitative conclusions.

Note that the condition (14) is fulfilled when $x_1=x_{1cr}$, where

$$x_{1cr}=\frac{\beta}{(\alpha+\sigma)}\approx\frac{\beta}{\alpha}\approx 1.8\times10^7\ \mathrm{cm}^{-3}. \tag{17}$$

We see that the most rapid changes of both x_1 and x_2 are indeed associated with the moments of their nighttime drops as is noted in Sect. 3.1. The characteristic time of the most rapid changes of both x_1 and x_2 is of order 10^2 s, that is, it is two orders of magnitude less than that during the other stages of evolution.

The effective increase of the distance between the IPs belonging to closely spaced phase trajectories during the second stage of the nighttime evolution (see Sect. 3.1.2) is

conditioned not only by rapid changes of variable values but also by the discrepancy between the moments of the most rapid changes in different trajectories. As demonstrated in Appendix, to determine these moments, it is sufficient to consider Eq. (1) with the only term "$-\alpha x_2$" in the right-hand side (that is, neglecting the term "$-\mu x_1$").

According to the discussion of Sect. 3.2, the presence of the strong bend is believed to be one of the basic features of NEM, conditioning the possibility of CDB. As pointed out in Sect. 3.2, such a peculiarity is determined by the second stage of the nighttime evolution, and, hence, by the terms of the dynamic equations analyzed above.

Thus, the above analysis leads to the conclusion that the mechanism of CDB origination is based on the processes determined by the terms "$-\alpha x_2$" of (1) and "$-\beta x_2^2/x_1^2$" of (2). The first one provides self-acceleration of the relative changes of x_1, which, in turn, provides the conditions for the abrupt changes of x_2. The second term is directly responsible for abrupt changes of x_2, which are the most essential part of the mechanism of originating of CDB. Note that our control runs of the essential model with $\sigma=\mu=0$ have demonstrated the same regimes of CDB as those possessed by the "proper" essential model.

Note also that the comprehension of the role of different terms of Eqs. (1) and (2) appears to be especially important for prediction of results of possible modifications of the system due to involvement of additional chemical processes, or, with changes in the parameters values. The values of new terms and their roles should be compared with those of the basic terms defined above.

4.2 Analysis of the modeled chemical processes

As follows from the above analysis, the possibility of the CDB is conditioned by the processes of an almost linear (with time) decrease of x_1 during the first stage of the nighttime evolution and the consequent abrupt drop of the x_2 value during the second stage. These processes are shown to be due to the presence of the terms "$-\alpha x_2$" in (1) and the term "$-\beta x_2^2/x_1^2$" in (2). Below we analyze the chemical processes responsible for these terms.

Evidently, the term "$-\alpha x_2$" cannot be connected with a single ordinary chemical reaction, for a rate of such a reaction is always proportional to the concentration of the destroyed species. For example, the continuity equation for reagent X reacting with reagent Y in the bimolecular reaction of the type

$$X + Y \rightarrow \text{products}$$

must be written as follows:

$$\frac{d(X)}{dt} = -k(X)(Y),$$

where k is a reaction rate constant. We notice that in this case the rate of relative changes of reagent X does not depend on X and, thus cannot increase with time as in the case of (1), unless the concentration of reagent Y increases.

However, Eq. (1) is not an ordinary continuity equation, but a specific approximate equation describing the "slow" changes of atomic oxygen (see Sect. 2, and FKM). The origin of this term is caused by joint processing of the reactions (R4), (R5), and (R6).

$$HO_2 + O \rightarrow OH + O_2 \quad \text{(R5)}$$
$$OH + O \rightarrow H + O_2 \quad \text{(R4)}$$
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{(R6)}$$
$$2O \rightarrow O_2.$$

These three reactions form the known catalytic cycle destroying atomic oxygen (see, e.g., Brasseur and Solomon, 1984). The main distinctive feature of this cycle under the mesospheric conditions is that the rate of its processing does not depend on concentrations of the destroyed species, and depends only on concentration of the catalyst (atomic hydrogen). (OH and HO_2 can be considered as intermediate forms of the catalyst, their concentrations are defined as functions of concentration of H according to (4) and (5).) In other words, the peculiarity of the cycle is that it is "autonomous" relative to destroyed species. This peculiarity is conditioned by the fact that the rate limiting reaction of the cycle (reaction (R6)) does not involve atomic oxygen. Mathematically, independence of the rate of the atomic oxygen destruction on its concentration reflects the fact that concentrations of the "fast" variables (OH) and (HO_2) are inversely proportional to the concentration of O (see (4) and (5)).

If Eq. (1) involved the term $\alpha' x_2 x_1$ corresponding to the hypothetical single bimolecular reaction instead of the term "$-\alpha x_2$", it is rather obvious that evolution of the system would be much smoother, and, thus, an essential part of the mechanism of originating of CDB, connected with the presence of the stage of abrupt changes of variables, would vanish. Indeed, control calculations with Eq. (1) changed in such manner have demonstrated only the presence of the period-1 solutions in a wide range of the parameter values. The magnitude of α' in these calculations has been chosen such that the daytime equilibrium variable values in the changed system should be equal to those in the "proper" system.

The term "$-\beta x_2^2/x_1^2$" in Eq. (2) appears due to the bimolecular reaction (R3) between OH and HO_2. It is important to note that the concentrations of both OH and HO_2 are determined by joint processing of the reactions (R4)-(R6) forming the catalytic cycle mentioned above, while the reaction (R3) provides irreversible destruction of the catalyst. Note also that the reaction (R3) does not involve the catalyst in its major form (atomic hydrogen) but only short lived intermediate forms OH and HO_2 which react with the species destroyed in the catalytic cycle (atomic oxygen). The noted facts condition the inverse proportionality of the net rate of the atomic hydrogen destruction to the square of the atomic oxygen concentration.

Hence, we can conclude that this is a catalytic cycle, characterized by independence of its processing rate on concentration of the destroyed species, that can be considered as the major chemical peculiarity facilitating appearance of CDB of the mesospheric PCS. The revealed role of this peculiarity gives us grounds to refer to it as to

the chemical mechanism responsible for the mesospheric PCS instability under periodic parametric modulation. By the instability we mean both the behavior of the system in the chaotic regime and the loss of stability of the periodic solutions. In this sense, the role of the discussed peculiarity in our system with periodically modulated parameters is similar to the role of autocatalytic processes for chemical systems with time-independent parameters. The autocatalysis is inherent almost in all chemical systems demonstrating chemical instabilities (see, for example, Field and Burger, 1985). The autocatalysis seems to be responsible also for the known examples of the chemical instabilities of the atmospheric PCSs. In particular, Heicklen et al. (1971) revealed an autocatalytic process in tropospheric PCS; Feigin and Konovalov, (1995, 1996) demonstrated that autocatalytic processes are responsible for the instability of the Antarctic PCS. An evident role of autocatalysis is that it provides possibility for an exponential increase of small perturbations of the equilibrium concentration of reagent. The catalytic cycle (R4)-(R6) alone does not provide the possibility of an exponential increase of perturbation of stable periodic variations but it is an essential part of the mechanism providing this possibility. An exponential (on the average) increase of perturbations of any periodic solution can convert this solution to the chaotic one. So, the revealed role of the cycle (R4)-(R6) and the discussed analogies suggest that the presence of similar "autonomous" cycles in other atmospheric PCSs may indicate that these systems too can possess CDB under appropriate conditions.

We can conclude that from the viewpoint of chemistry the dominant role in the processes responsible for the appearance of CDB in the mesospheric PCS belongs to the catalytic cycle (R4)-(R6) characterized by independence of the rate of its processing on concentration of the destroyed species, and to the reaction (R3) causing destruction of the catalyst and involving only short lived species of the catalytic cycle immediately reacting with the species destroyed in the cycle.

5 Concluding remarks

The goal of this paper was to reveal the origin of complicated dynamic behavior (CDB) of the mesospheric photochemical system (PCS) model by Fichtelmann and Sonnemann (1992) forced by diurnal variations of the photolysis rates. By the "origin" we mean here the peculiarities of the evolution of the system within a single period of parametric modulation and those of the chemical processes involved in the model, that are significant for CDB appearance, as well as the mechanisms determining the significance of the pointed peculiarities for the CDB appearance.

For this purpose we have employed the essential dynamic model of the mesospheric PCS elaborated by Feigin et al., (1998), which demonstrates the same possibilities of the dynamic behavior as the significantly more complicated original model.

We have shown that the essential peculiarities of the system evolution within a unit period of modulation which are responsible for CDB are (1) the presence of the stage of abrupt changes of variables during the nighttime evolution, and (2) the humped structure of the night evolution mapping for atomic hydrogen, which is the dependence of the atomic hydrogen concentration at the end of the night on that at the beginning of the night.

The catalytic cycle characterized by independence of the atomic oxygen destruction rate on its concentration has been found to be the principal chemical peculiarity of the system provoking the CDB appearance.

We have studied the mechanisms of CDB appearance using two different approaches that complement each other. From the viewpoint of the first approach the mechanism of CDB appearance can be presented as the consequence of the processes causing the exponential (on the average) growth of perturbation of the solution with time. The essential part of the mechanism is connected with the stage of abrupt changes of component concentrations during the nighttime evolution. In the context of the other approach, the mechanism of CDB appearance can be described by means of Poincaré mapping. We have shown that the main dynamic properties of both the original and essential dynamic models are reproduced by a mere one-dimensional mapping, and we argue that the mechanism of originating of CDB in the mesospheric PCS is essentially similar to that described by Feigenbaum (1978).

On the basis of results of qualitative analysis we have derived an analytical expression (see Appendix) for estimation of the parameter values under which CDB occurs.

We believe that results of this study will promote further investigations into the nonlinear nature of the atmospheric PCSs. In particular, they may significantly simplify the investigations aimed at revealing CDB of the real mesospheric PCS, as the results obtained allow one to estimate the action of various factors existing in the real mesosphere, which are not taken into account in the photochemical models, on the mesospheric PCS behavior. The important role of the catalytic cycle characterized by independence of the net rate of the species destruction on its concentration points the direction for searching other atmospheric PCSs possessing CDB under periodic parametric modulation. We suppose that the presence of a similar cycle in other PCSs indicates that these systems may possess CDB under appropriate conditions. Besides, as follows from Sect. 3.2, the presence of such a cycles can indicate an extreme sensitivity of a certain dynamic process in the system to the initial conditions of this process or the system parameters. Although identification of such cycles is above the scope of this paper, we can point as an example to the cycle suggested by Molina et al. (1987) for the conditions of the polar lower stratosphere:

$$2\times(Cl+O_3\rightarrow ClO+O_2)$$
$$ClO+ClO+M\rightarrow Cl_2O_2+M$$
$$Cl_2O_2+h\nu\rightarrow ClOO+Cl$$
$$\underline{ClOO+M\rightarrow Cl+O_2}$$
$$2O_3\rightarrow 3O_2.$$

The rate limiting reaction here is a reaction of ClO-dimer formation (Anderson et al., 1989) which does not involve an ozone destroyed in the cycle. The other possible cycle is the one that plays a significant role in the lower middle-latitude stratosphere (Brasseur and Solomon, 1984):

$$\begin{aligned} &ClO+HO_2 \rightarrow HOCl+O_2 \\ &Cl+O_3 \rightarrow ClO+O_2 \\ &HOCl+h\nu \rightarrow Cl+OH \\ &\underline{OH+O_3 \rightarrow HO_2+O_2} \\ &2O_3 \rightarrow 3O_2. \end{aligned}$$

The rate limiting reaction of this cycle is the upper reaction. The presence of such cycles indicates that the lower stratospheric PCS may possess CDB. The necessary parametric modulation may be connected with seasonal variations of the photolysis rates and the rates of heterogeneous reactions.

Using the mesospheric PCS as an example we have shown that computation of the mapping connecting the initial and final values of any dynamic process observed in the atmospheric PCS can provide valuable information about the nonlinear nature of this PCS, as well as indications which types of CDB and under what conditions can be expected for these PCS. We emphasize that the humped structure of the mapping, especially accompanied by its strong bend, can bear evidence that such a system may be strongly sensitive to deviations of its parameter values. The above suggestions are especially valuable while predicting the changes in the atmospheric PCSs caused by the trends of the atmospheric parameters.

Appendix
The criterion of CDB of the mesospheric PCS

Below we derive approximate analytic expressions defining the region of the parameter values under which the CDB occurs. In other words, below we obtain an approximate criterion of CDB of the mesospheric PCS. Derivation of the criterion advances the comprehension of the origin of CDB. Besides, the criterion can be used to estimate where and when CDB of the real mesospheric PCS is possible. Below we briefly describe the focal points of the procedure of the criterion derivation.

As the basis for the derivation we use the following facts established in the previous sections:

1. The possibility of CDB is conditioned by the presence of deep nighttime drops of variable values.
2. When CDB takes place, the time interval (τ_d) from the beginning of the nighttime evolution till the moment of the nighttime drop is approximately equal to the duration of the nighttime stage of the evolution (T_n). To put this another way, the boundaries of the interval of the control parameter r ($r_{min}<r<r_{max}$), corresponding to CDB, is determined by the following condition:

$$\tau_d \approx T_n. \qquad \text{(A1)}$$

3. The duration of the daytime evolution (T_d) when CDB occurs is smaller than the characteristic time (τ_e) of damping of perturbations from the daytime equilibrium state. An expression determining this characteristic time was found in FKM:

$$\tau_e = \frac{\delta}{\alpha \gamma r}. \qquad \text{(A2)}$$

Using (A2) the condition (3) can be formulated as follows:

$$T_d < \frac{\delta}{\alpha \gamma r}. \qquad \text{(A3)}$$

The characteristic value of τ_d can be estimated under the assumptions that the x_2 value does not change until the moment of the nighttime drop, and the nighttime drop itself takes place at the moment when the x_1 value under such an assumption becomes zero. These assumptions appear to be reasonable since, as is noted in Sect. 4.1, the relative changes of x_2 before the moment of the nighttime drop are small in comparison with those of x_1, and the moment of the nighttime drop is indeed associated with extremely small value of x_{1cr} (see (15)). According to these assumptions and using Eq. (1) we find:

$$\tau_d \approx \frac{x_1}{\alpha\, x_{2in}^{in}}, \qquad \text{(A4)}$$

where x_{1in} and x_{2in} are the variable values initial for the nighttime evolution. The validity of the obtained estimation is corroborated by Fig. A1 which shows numerically calculated dependences of τ_d on x_{2in} for different values of x_{1in} (solid curves) in comparison with the estimation (A4) (dashed curves).

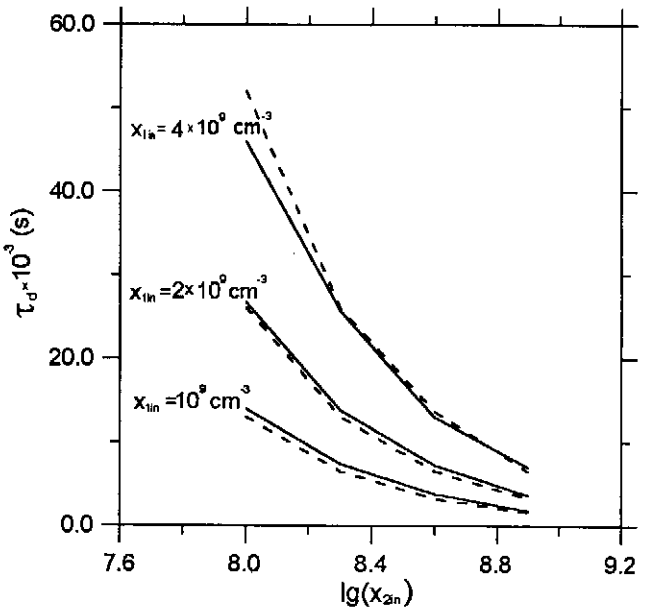

Fig. A1. The dependences of duration of the nighttime evolution (τ_d) until abrupt drops of variables on the values of x_2 initial for the nighttime evolution, calculated numerically (solid lines) and estimated (dashed lines). Different curves correspond to different values of the initial values of x_1.

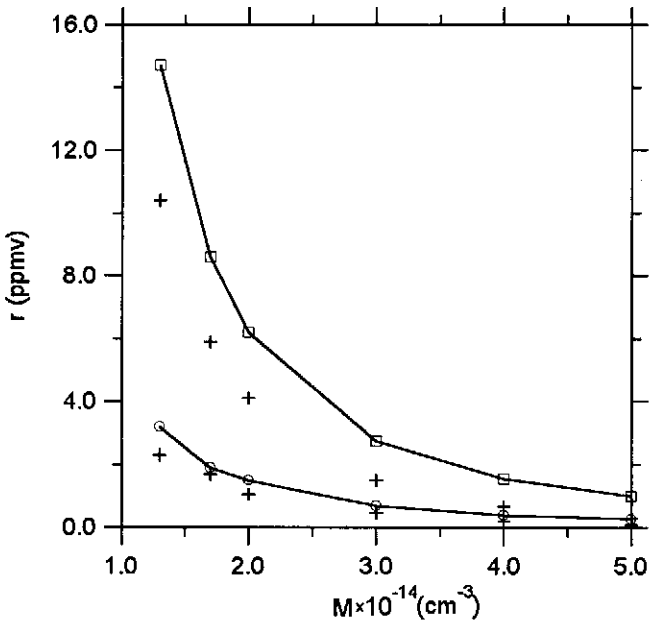

Fig. A2. The dependences of the parameter r values bounding the region of nonlinear dynamic behavior on the value of air concentration (M). The values found by means of numerical calculations are shown by the crosses and the ones estimated according to equations (A5)-(A7) are shown by the lines with circles (for r_{min}) and squares (for r_{max}).

To determine the dependences of x_{1in} and x_{2in} on r and thus to determine, using (A1), (A3) and (A4), the boundary values r_{min} and r_{max}, we consider the period-1 solution outside the region of CDB, that is for $r<r_{min}$ and $r>r_{max}$. To determine r_{min} we derive, first, the analytical solution of the set (1)-(3), which is strictly valid when $r<<r_{min}$, and the dynamic process is manifested as small (linear) oscillations about a certain mean equilibrium state ($\bar{x}_{1,2}$). Then, we make an assumption that the obtained expressions are approximately valid when $r\sim r_{min}$. As a result, we find

$$r_{\min} \approx \frac{2(\bar{x}_1 - \alpha T_n \bar{x}_2) + \delta T_n}{\alpha\gamma T_d T_n}, \qquad \text{(A5)}$$

where $\bar{x}_1 = \dfrac{T\sigma x_2^{-2}}{T_d \gamma r}$, and

$$\bar{x}_2 = -\frac{\alpha\gamma r T_d}{2\sigma\mu T_n} + \sqrt{\left(\frac{\alpha\gamma r}{2\sigma\mu}\right)^2 + \frac{T_d^2 \delta\gamma r}{T T_n \sigma\mu}}.$$

The value of r_{max} equals the smallest of r^d_{max} and r^n_{max}, which are defined by the conditions (A3) and (A1), respectively. From (A3) we immediately obtain:

$$r^d_{\max} = \frac{\delta}{\alpha\gamma T_d}. \qquad \text{(A6)}$$

The rough consideration of the period-1 solution under the condition $r>r_{max}$ and the assumption that (A3) is valid gives the following expression for r^n_{max}, which is similar to (A4):

$$r^n_{\max} = \frac{\delta}{\alpha\gamma T_n}. \qquad \text{(A7)}$$

So the r_{max} value is restricted by the stage (the daytime, or nighttime) of the evolution with the largest duration.

The dependences of r_{min} and r_{max} on the concentration of the air molecules (M), which is another parameter of the system, calculated in accordance with (A5) and (A6), are shown in Fig. A2 by the lines with circles and squares, respectively. (Note that since we assume $T_d=T_n$, the expressions (A6) and (A7) are equivalent.) The corresponding values of r_{min} and r_{max} calculated numerically using the essential dynamic model are shown by crosses. Recall that we use $M=1.7\times10^{14}$ cm^{-3} throughout this paper. Modest changes of this parameter can be interpreted as the changes of the height of the location of the modeled PCS. We can conclude that the analytic estimations (A5)-(A7) yield the boundaries of the CDB which are in satisfactory agreement with the ones calculated rigorously.

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